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# Low Cost Fabrication of Silicon Carbide Based Ceramics and Fiber Reinforced Composites

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BASED CERAMICS AND FIBER REINFORCED  
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# **Low Cost Fabrication of Silicon Carbide Based Ceramics and Fiber Reinforced Composites**

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## **ABSTRACT**

A low cost processing technique called reaction forming for the fabrication of near-net and complex shaped components of silicon carbide based ceramics and composites is presented. This process consists of the production of a microporous carbon preform and subsequent infiltration with liquid silicon or silicon-refractory metal alloys. The microporous preforms are made by the pyrolysis of a polymerized resin mixture with very good control of pore volume and pore size thereby yielding materials with tailorable microstructure and composition. Mechanical properties (elastic modulus, flexural strength, and fracture toughness) of reaction-formed silicon carbide ceramics are presented. This processing approach is suitable for various kinds of reinforcements such as whiskers, particulates, fibers (tows, weaves, and filaments) and 3-D architectures. This approach has also been used to fabricate continuous silicon carbide fiber reinforced ceramic composites (CFCCs) with silicon carbide based matrices. Strong and tough composites with tailorable matrix microstructure and composition have been obtained. Microstructure and thermomechanical properties of a silicon carbide (SCS-6) fiber reinforced reaction-formed silicon carbide matrix composites are discussed.

## **INTRODUCTION**

Silicon carbide based advanced ceramics and fiber reinforced composites are leading candidate materials for a number of applications in aeronautics, energy,

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electronics, nuclear, and transportation industries [1-3]. In the aeronautical arena, these materials are being considered for applications in hot sections of jet engines such as the combustor liner of the high speed civil transport (HSCT). Rocket nozzles and reentry thermal protection systems are among other potential aerospace applications. Applications in the energy industries include radiant heater tubes, heat exchangers, heat recuperators, and components for land based turbines for power generation. These materials are also being considered for use in the first wall and blanket components of fusion reactors, in furnace linings, and bricks, and are being used as components for diffusion furnaces (boats, tubes) in the microelectronics industry.

There are a number of critical issues related to commercially available silicon carbide ceramics and fiber reinforced composite materials. Fabrication by current processing techniques of complex shape components of near net shape is very expensive, and even then many desirable properties are not achievable. Typical problems associated with reaction bonding are the excessive amount of free silicon (~15-40 vol%) and presence of sintering aids in some sintered materials. The coarsely distributed free silicon and sintering aids in commercially available silicon carbides degrade high temperature properties. On the other hand, fiber reinforced silicon carbide matrix composites available commercially at present are produced by the chemical vapor infiltration (CVI) process. The CVI processing time is typically hundreds of hours, with multiple process interruptions to machine off the surface case in order to expose the interior to further infiltration. The final material contains about 10-15% residual porosity. The long processing time and intermediate machining steps contribute to the high cost of components made by the CVI process.

At NASA Lewis, a low cost processing technique for the fabrication of silicon carbide-based advanced ceramics and composites has been developed which requires significantly less fabrication times and/or processing temperatures than current processing techniques. The products produced by this process are fully dense, have tailorable microstructure and mechanical properties, and can incorporate second phases without the detrimental effects of unwanted sintering aids [4-10]. This process consists of the production of a microporous carbon preform and its subsequent infiltration with liquid silicon or silicon-refractory metal alloys. The microporous preforms are made by the pyrolysis of a polymerized resin mixture. Pore volume and pore size are carefully tailored to control the size and distribution of the final constituents [5-8]. This process produces silicon carbide based ceramics at low cost and has near-net and complex shape capabilities.

This processing approach has been used to fabricate ceramic matrix composites with silicon carbide based matrices and is suitable for various kinds of reinforcements such as whiskers, particulates and continuous fibers (tows, weaves, and filaments). Various



types of fiber reinforcements i.e., carbon, alumina and silicon carbide has been used as reinforcements in this process. It can also be used to fabricate composites with 3-D architectures. Key properties such as strength and toughness, creep, and environmental and thermal shock resistance of these materials can be tailored.

The work reported here is part of a program aimed at developing low cost, near-net and complex shape components of reaction-formed silicon carbide based ceramics and composites with tailorable microstructure and thermomechanical properties. In this paper, fabrication process and advantages of using these materials in various applications will be presented. Mechanical properties (elastic modulus, flexural strength, and fracture toughness) of three reaction formed silicon carbide materials will be discussed. The microstructure and mechanical behavior of silicon carbide (SCS-6) fiber reinforced composites fabricated by this process will also be presented.

## PROCESS DESCRIPTION

A schematic description of the reaction forming of silicon carbide based ceramics and composites is given in Fig. 1. This process consists of the production of a microporous carbon preform and its subsequent infiltration with liquid silicon or silicon-refractory metal alloys [4-8]. The microporous preforms are made by the pyrolysis of a polymerized resin mixture. The pyrolysis process affords excellent control of pore volume, pore size and distribution. The silicon or silicon-refractory metal alloy infiltration of the preforms and reaction of liquid silicon with carbon, yields silicon carbide based ceramics with tailorable microstructure and composition. Alloying silicon with refractory metals reduces the amount of residual silicon phase. Materials with controllable amount of silicon or other phases (4-40%) can be obtained.

The precursor materials (resin, pore formers, etc.) for microporous carbon preforms are inexpensive (\$2/lb) and can be handled under normal laboratory conditions without any special equipment. Silicon in lump form is also inexpensive e.g., 6N pure electronic grade silicon lumps can be bought for \$10-12/lb. If metallurgical grade or other type of silicon is used for infiltration, the final material cost will be further reduced.

All the mechanical property data reported in this paper are for ceramics formed by the reactive infiltration in to identical microporous carbon preforms of molten silicon (NSC-20), silicon-1.7 at% molybdenum (NSC-21) and silicon-5 at% niobium (NSC-22) alloys. The details of microporous carbon preform fabrication and other infiltration conditions have been described elsewhere [5-8]. The control of processing conditions is critical to avoid microstructural coarsening, silicon vein and lake formations, and cracking due to thermal expansion mismatch and volume change. After infiltration, samples were



cross-sectioned and polished for metallographic studies. Powder x-ray diffraction analysis was used to identify different phases in the reaction-formed materials.

## **TAILORABLE SILICON CARBIDE CERAMICS**

### **Microstructure**

An optical micrograph of the NSC-20 material, fabricated by silicon infiltration of carbon preforms, is given in Fig. 2. Complete conversion of carbon to silicon carbide and the uniform distribution of a silicon phase (white) throughout a silicon carbide matrix (grey) are evident in Fig. 2. Similar microstructures were obtained for the silicon-1.7 at% molybdenum and silicon-5 at% niobium alloy infiltrated materials. The free silicon content of the NSC-20 material was ~10%, significantly lower than the silicon content (~20-30%) of commercially available reaction-bonded silicon carbide materials. The amount of residual silicon in the silicon-alloy infiltrated materials is less than that in the material made using silicon infiltration due to the formation of refractory disilicides.

### **Mechanical Properties**

#### ***Elastic Modulus***

Elastic moduli data for reaction-formed silicon carbide ceramics along with some commercial silicon carbides are given in Fig. 3. Moduli data for the commercial silicon carbides were taken from the literature [12-13]. The elastic modulus of silicon containing silicon carbide material (NSC-20) is 360 GPa which is comparable to REFEL-1 and Coors SC-2, but lower than NC-203 (450 GPa). There is no significant difference in the modulus of NSC-20 (360 GPa) and NSC-21 (347 GPa), which may be due to the low amount of molybdenum disilicide in the NSC-21 material. In addition, the modulus of molybdenum disilicide is comparable to that of silicon carbide (427 GPa). The modulus value of NSC-22 is 292 GPa, somewhat lower, probably due to presence of niobium disilicide (300 GPa) and silicon.

#### ***Flexural Strengths***

The flexural strengths of silicon infiltrated reaction-formed material (NSC-20) along with two commercial silicon carbides as a function of temperature are presented in Fig. 4. The average room temperature strength of silicon infiltrated material (NSC-20) is  $371 \pm 28$  MPa. The data points represent mean results for ten tests at room temperature and five tests at elevated temperatures. In general, flexural strengths of NSC-20 are higher than two commercial silicon carbides. The apparent increase in strength at 1100 °C may be due to



healing of machining damage. Further experimental studies are in progress to confirm this hypothesis.

### ***Fracture Toughness***

The room temperature fracture toughness of these materials, determined using the single-edge-precracked-beam (SEPB) method, is given in Fig. 5. The fracture toughness of silicon-5 at% niobium alloy infiltrated material (NSC-22) is  $3.7 \pm 0.3 \text{ MPa m}^{1/2}$  while for the silicon infiltrated material (NSC-20) it is  $2.5 \pm 0.2 \text{ MPa m}^{1/2}$ . This difference in the fracture toughness of two ceramics can be explained on the basis of the thermal expansion coefficients of the different phases. The toughening mechanism in the silicon-alloy infiltrated material may be crack deflection by thermal residual stress field which develops around refractory disilicide and silicon particles upon cooling due to thermal expansion mismatch [12]. The thermal expansion coefficients of molybdenum disilicide ( $8.2 \times 10^{-6}/^{\circ}\text{C}$ ), niobium disilicide ( $11.7 \times 10^{-6}/^{\circ}\text{C}$ ) and silicon ( $7.63 \times 10^{-6}/^{\circ}\text{C}$ ) are higher than  $\beta$ -silicon carbide ( $4.4 \times 10^{-6}/^{\circ}\text{C}$ ), the refractory disilicide and silicon particles are under isostatic tensile stresses. These thermal expansion mismatches impart radial tensile and tangential compressive stresses to silicon carbide matrix. This could lead to crack deflection around second phase particles.

## **FIBER REINFORCED COMPOSITES**

The reaction forming process has also been used to fabricate continuous fiber reinforced ceramic composites (CFCCs) with silicon carbide based matrices. This process is suitable for various kinds of reinforcements such as whiskers, particulates and fibers (tows, weaves, and filaments) as well as 3-D architectures. The microstructure and thermomechanical properties of the silicon carbide based ceramics and composite materials produced by this process can be tailored to suit design and application requirements. Key properties such as high strength and toughness, creep, environmental and thermal shock resistance of these materials can also be tailored and will be discussed in the following sections.

### **Microstructure**

The silicon carbide fiber-reinforced silicon carbide matrix composites produced by the reaction forming process are fully dense. The liquid silicon or silicon alloy infiltration time is relatively short (15 minutes to one hour) in contrast to the long times (several days) required for the chemical vapor infiltration process. An optical micrograph of silicon carbide (SCS-6) fiber reinforced-silicon carbide matrix composites is given in Fig. 6. This



micrograph shows uniform microstructure with no unreacted carbon or porosity. One important point to note here is the protection afforded by the coating on as received SCS-6 fibers. Various investigators have used 4-5  $\mu\text{m}$  barrier coatings to prevent molten silicon attack on these fibers. These additional coating applications complicate processing and handling, and add extra cost to composite manufacture. Dense composites have also been obtained with small diameter woven fiber composites.

### **Mechanical Properties**

The stress-displacement behavior of a SiC(SCS-6) fiber-SiC matrix composite is given in Fig. 7. This composite has been tested in four-point bending at room temperature. The unidirectional composites with ~17 percent by volume of fibers have a first matrix cracking stress above 262 MPa (38 ksi). The load-displacement curve shows a non-linear behavior with a graceful failure. The interfacial shear strength of this composite is in the range of 30-60 MPa depending on the processing time, temperature and the infiltrant composition. Detailed thermomechanical and thermochemical characterization of these composites under the hostile environments to be encountered in engine applications is underway.

### **Thermal Properties**

Unidirectional composites made with SiC(SCS-6) fibers have also been tested in burner-rig thermal shock tests. In this test, a hot flame is impinged on the surface of a 2"X3" composite and the temperature at the back surface is measured by pyrometer. The data for a variety of materials and the temperature difference between the front and back surface is given in Fig. 8. The NCC-20 material made by the process described above has the lowest  $\Delta T$  indicating highest thermal conductivity.

## **ADVANTAGES**

The silicon carbide based ceramics, produced by the reaction forming process, have very good phase distribution and morphology. Materials with low levels of free silicon (<4-5 vol%) have been produced. The amount of free silicon can be further reduced by silicon-refractory metal alloy (molybdenum or niobium) infiltrations. This process is low cost with near-net and complex shape capabilities.



The silicon carbide fiber-reinforced silicon carbide matrix composites produced by this process are fully dense. The liquid silicon or silicon alloy infiltration time is relatively short (15 minutes to one hour) rather than the long times (several days) required for the chemical vapor infiltration process.

## **NEAR TERM AND FUTURE APPLICATIONS**

### **Aerospace Applications**

The principal application of this technique is to fabricate near-net and complex shaped silicon carbide based ceramic and composite components for aeronautics and space applications. It is expected that these materials will find applications in the hot section of jet engines; for example, the combustor liner of the proposed high speed civil transport (HSCT). The combustor liner requires a material which is non-porous, has high thermal conductivity and is resistant to degradation in both rich- and lean-burn combustion environments. Another area of application for these silicon carbide based materials is in the thermal protection systems of reentry vehicles and high speed aircraft, where materials that can withstand the high temperatures and thermal gradients generated by the high speeds are required.

The silicon carbide based multiphase ceramics containing different phases such as  $\text{MoSi}_2$ ,  $\text{NbSi}_2$  and others are candidate material for space shielding applications. These materials can outperform conventional armor materials. There is considerable interest in light weight shields to protect spacecraft and bases from debris and micrometeorites for the Space Station and other proposed manned missions back to Moon and on to Mars.

### **Terrestrial Applications**

Silicon carbide based ceramic and composite materials fabricated using this technique will have a variety of applications in the energy industries. These applications include radiant heater tubes, heat exchangers, heat recuperators, various components for land based turbines for power generation, transportation (automobiles and trucks), and energy conversion devices. The excellent oxidation resistance of silicon carbide based materials offer alternative possibilities in the low temperature range as condensing heat exchangers. The main stumbling block for these applications has been the high cost of components fabricated to near-net and complex shape.

In nuclear industries, these materials are under consideration for use in the first wall and blanket components of a fusion reactor. Conventionally sintered silicon carbide



materials, apart from being costly, contain sintering aids such as boron which lead to volume swelling upon irradiation. On the other hand, commercially available SiC/SiC composites, produced by CVI, contain 15-20% of residual porosity and are quite expensive. The materials produced by the process reported here contain no sintering aids. SiC/SiC composites have been produced with virtually no porosity (theoretically dense). The application of reaction-formed silicon carbide materials in the high radiation environment of fusion reactors can provide a very low activation system. This will significantly reduce waste disposal and maintenance problems and environmental and safety concerns.

Conventional monolithic silicon carbide ceramics need high sintering temperatures which drives their cost up. For their toughness improvement, various phases have to be hot pressed together. In this technique, second phases for toughening have been produced in-situ. The improved fracture toughness along with other properties makes these materials a strong candidate for armor applications. In addition, the near-net shape capabilities of this process can be used to produce materials for cutting tool applications.

Due to its high strength, excellent thermal shock resistance, and good oxidation resistance, silicon carbide based ceramics are being considered for furnace linings, bricks and other components in furnaces. Another area where low cost silicon carbide materials are desired is in the aluminum industry for reduction cells. The major requirements for the refractories for these applications are their structural and chemical stability over the entire cathode temperature range during cell start-up and operations. Silicon carbide based ceramics are ideal materials due to their excellent resistance to air oxidation, thermal shock tolerance and good resistance to molten salts.

## CONCLUSIONS

A method to produce silicon carbide-based high performance ceramics and composites which requires fabrication times and/or processing temperatures significantly less than other processing techniques such as chemical vapor infiltration, reaction sintering, pressureless sintering, hot pressing, and hot isostatic pressing has been developed at NASA Lewis. The products produced by this process are fully dense, with excellent control of microstructure, second phases and mechanical properties and without the detrimental effects of sintering aids. In addition, the materials produced by this process are low cost.

The near-net and complex shape capabilities, low processing time and temperature, and low cost will make the materials produced by this process affordable in a variety of applications. The advantages and benefits of using these materials for various components



## REFERENCES

- [1] D.C. Larsen, J. Adams, L. Johnson, A. Teotia, and L. Hill, "Ceramic Materials for Heat Engines," Noyes Publications, NJ (1985).
- [2] E. Fitzner and R. Gadow, Am. Ceram. Soc. Bull., 65, 2 (1986) 325-35.
- [3] E.E. Huccke, AMMRC Report TR-83-5, January 1983.
- [4] D.R. Behrendt, M. Singh and R.F. Dacek, 16th Conf. on Metal, Carbon and Ceramic Matrix Composites, NASA CP-3175 (1992) 695-705.
- [5] M. Singh and D.R. Behrendt, NASA-TM-105860 (1992).
- [6] M. Singh and D.R. Behrendt, J. Mater. Res., 9, 7 (1994) 1701-1708.
- [7] M. Singh and D.R. Behrendt, Mater. Sci. Eng., A187 (1994) 193-200.
- [8] M. Singh and D.R. Behrendt, Mater. Sci. and Eng., A194 (1994) 193-200.
- [9] D.R. Behrendt and M. Singh, J. Mater. Synth. Process., 2, 2 (1994) 133-139.
- [10] D.R. Behrendt and M. Singh, NASA-TM-106414 (1993).
- [11] Y-M. Chiang, R.P. Messner, C. Terwilliger, and D.R. Behrendt, Mater. Sci. Eng. A 144, (1991) 63-74.
- [12] M. Singh, R. Pawlik, J.A. Salem and D.R. Behrendt, Ceramic Trans. Vol 38, 'Advances in Ceramic Matrix Composites', Edited by N.P. Bansal, The American Ceramic Society, Westerville, OH (1993) 349-360.
- [13] Ceramic Source, Vol. 7, American Ceramic Society, Westerville, OH (1991) 313.



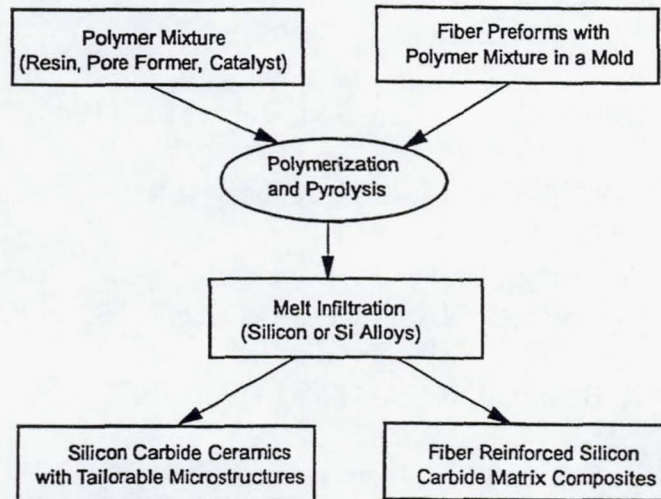


Figure 1.—Process flow chart for the fabrication of silicon carbide based ceramics and fiber reinforced composites.

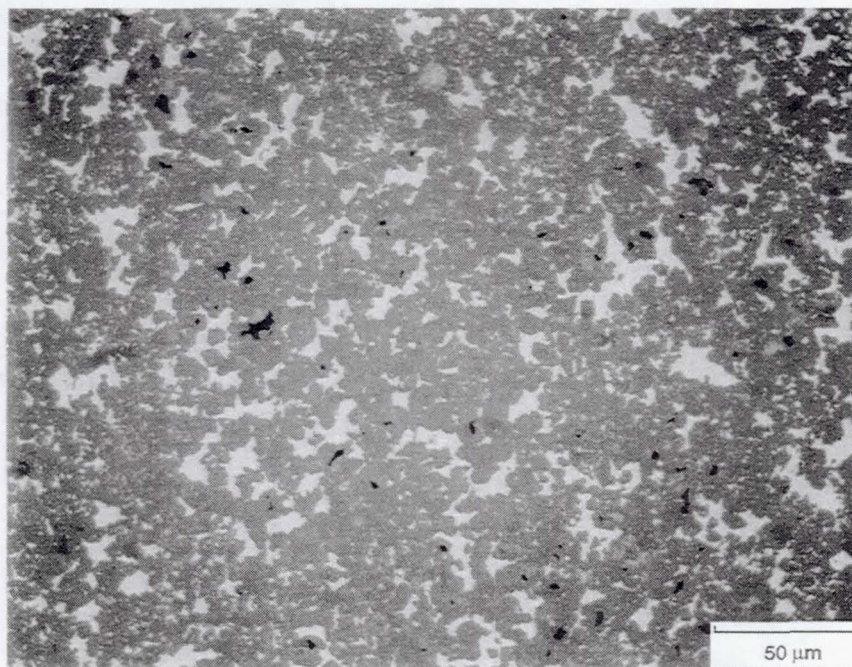


Figure 2.—Microstructure of reaction-formed silicon carbide (NSC-20) (Si is white and SiC is grey, x 400).



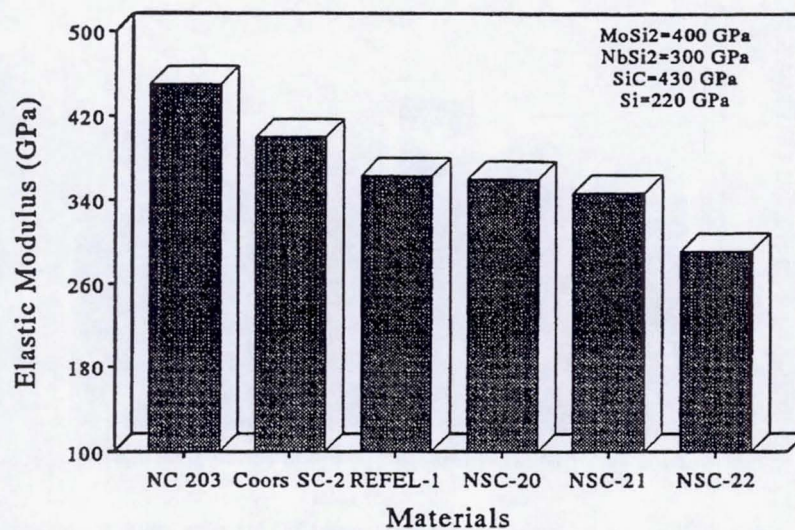


Figure 3.—Elastic properties of reaction-formed silicon carbide ceramics and other commercial materials.

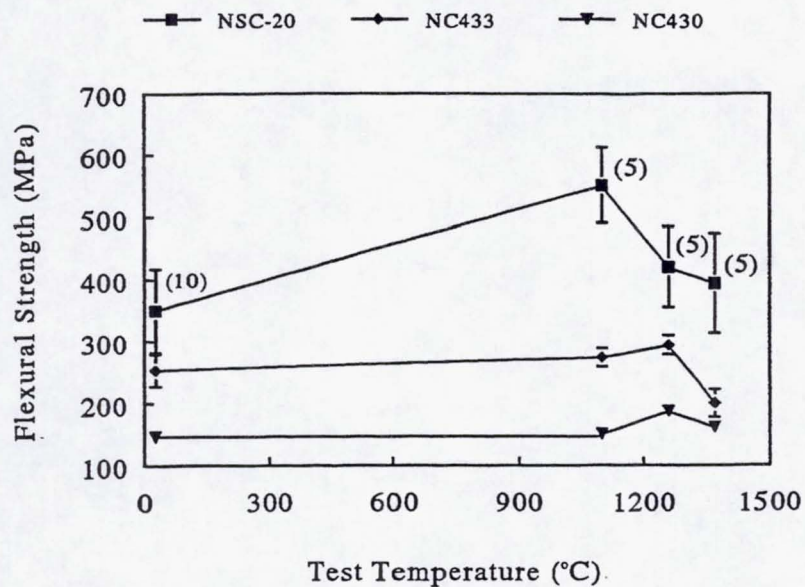


Figure 4.—Flexural strengths of reaction-formed SiC (NSC-20) and two commercial SiC as a function of temperature.



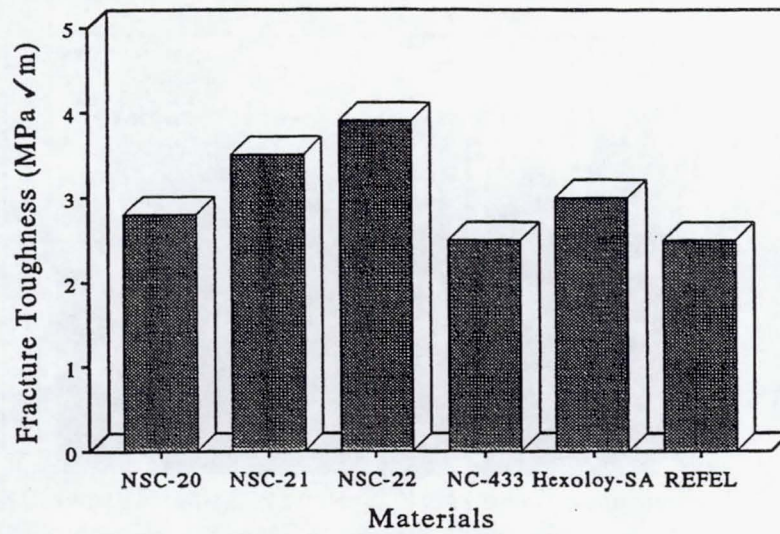


Figure 5.—Fracture toughness of reaction-formed SiC ceramics and commercial SiC at room temperature.

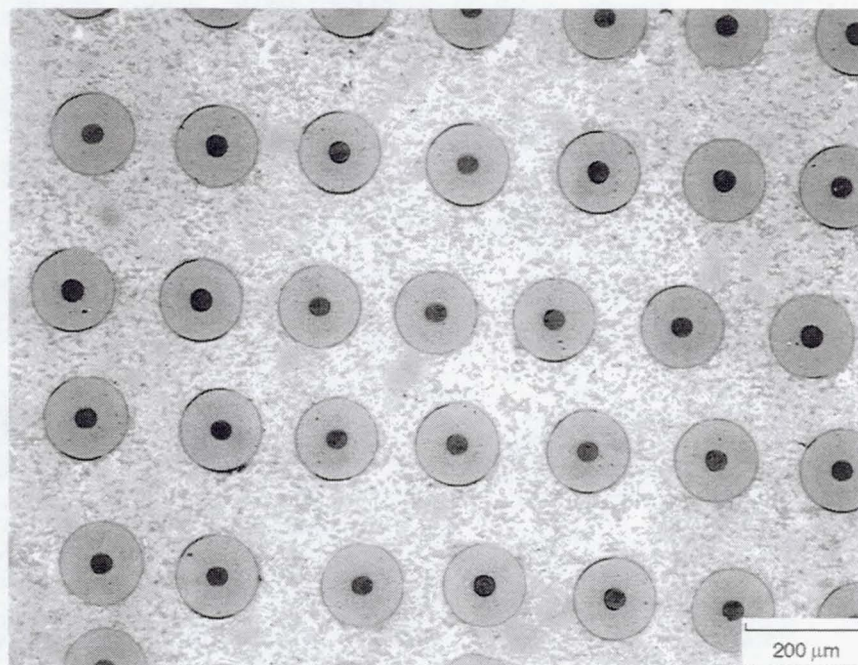


Figure 6.—Optical micrograph of a SiC (SCS-6)/SiC matrix composite.



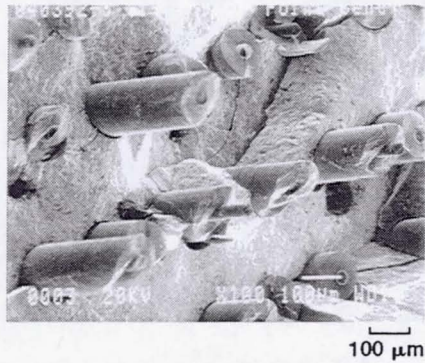
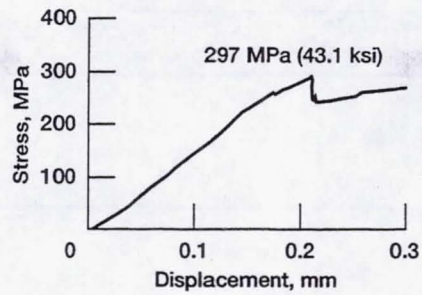


Figure 7.—Stress-displacement behavior and fracture surface of SiC (SCS-6) fiber-SiC matrix composites.

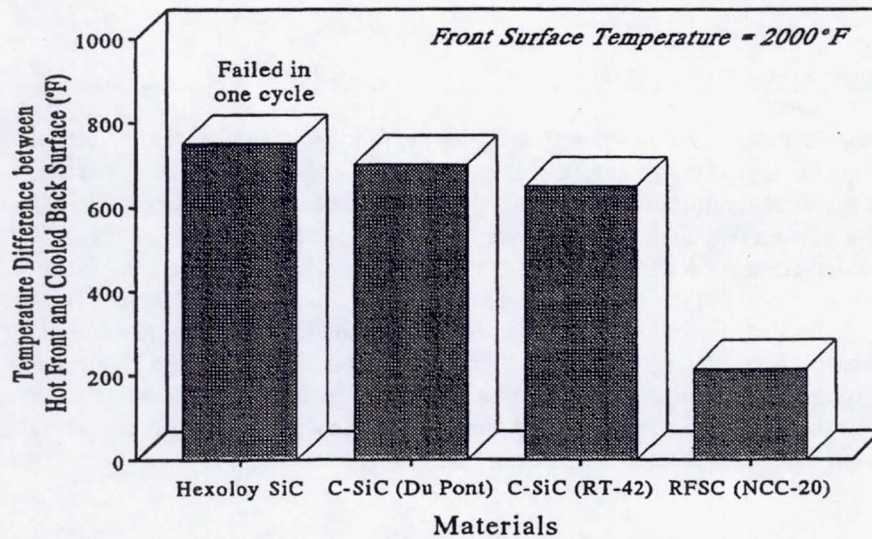


Figure 8.—Thermal properties of SiC (SCS-6)/SiC composites under burner rig tests.



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